

sorption is expected to shift towards shorter wave length, just like enole ethers. In fact 265 m μ band of acetoacetic ester is shifted to 245 m μ in copper chelate. That a structure like II also makes its contribution in I is shown by the existence of a weak band at 240 m μ in chelate I which is absent in legend. In salicyl aldehyde complex III there is no change in the absorption spectra evidently due to strong cross resonance. When compared with the absorption spectra of the salicyl aldehyde ion some change is noticed. The characteristic absorption of the ion at 380 m μ is absent in the chelate evidently due to fixation of the electron pair of the oxygen in phenolate ion.

Of late KOZO SONE attempted to correlate the stability of metal chelate with the shift in the absorption band of the legend⁴). Such correlation may not be possible in all cases. For example, for the three complexes mentioned the stability increases in the order III < II < I, but the spectral shift in I is positive, in II negative, while in III it is zero or strongly negative if the ion is considered. Further the corresponding nickel compounds gave absorption maxima at exactly the same positions as the copper complexes, although the stability was different in two cases. So it is evident that there is no systematic change in spectra with stability. In fact no such general relationship is expected. For, the shift in the absorption spectra is governed by the extent of mesomeric and electromeric effects, while stability also depends on coulombic effect and ionic size.

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¹) MARTELL and CALVIN: Chemistry of Metal Chelates Compounds. New York: Prentice Hall, Inc. 1952.

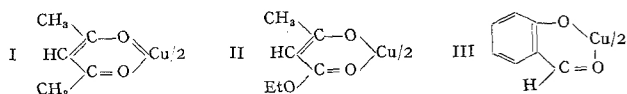
²) KIMBALL: J. Chem. Physics 8, 188 (1940).

³) CALVIN and BAILES: J. Amer. Chem. Soc. 68, 949 (1946).

⁴) KOZO SONE: J. Amer. Chem. Soc. 75, 5207 (1953).

Absorption Spectra of Copper and Nickel Chelates.

While considering the stabilities of copper complexes of acetylonyl acetone, acetoacetic ester and salicyl aldehyde CALVIN¹) proposed the following structures for these compounds.



The structure like I is theoretically quite feasible, since KIMBALL's calculation²) shows that the spatial disposition of copper AOs are favourable for the formation of a π -bond. In II and III although such structures are equally possible, strong cross resonance with ester group and phenyl nucleus respectively almost completely suppresses such structures with double bonded copper³).

The measurement of absorption spectra of these compounds in alcoholic solution is expected to furnish some conclusive evidence as to what extent such resonating forms contribute to the overall structure of these compounds; for, if copper π -bonds be in conjugation with $\alpha\beta$ unsaturated ketone as in I, the resonating path of the electron will be increased and the characteristic absorption band due to $\alpha\beta$ unsaturated ketone will shift towards longer wave length. In fact the 265 m μ band of the enole form of acetylonyl acetone is shifted to 295 m μ in copper complex. In acetoacetic ester since copper is not forming a π -bond no shift is expected in the characteristic absorption of enole form. But since the positively charged copper will strongly attract the lone pair of electrons of enolic oxygen with the consequent reduction of the resonating path of the electron in the enole form of acetoacetic ester, its characteristic ab-